Appl. No. 10/660,186                 Docket No. A01477
Amdt. dated July 03, 2007
Reply to Office Action of May 03, 2007

## REMARKS/ARGUMENTS

Claims 1-6 and 11-24 remain in this application. Claims 7-10 are cancelled without prejudice. No amendments to the claims are submitted at this time.

Response to rejection of claims 1-6, 11-20, and 22-24 over Irie

In the above-identified Office Action the Examiner rejected claims 1-6 and 11-20 under 35 USC §103(a) as being obvious over US 5,959,028 (Irie).

Applicants respectfully maintain that the Examiner has not provided a proper prima facie case for the recjection. Applicants respectfully maintain their arguments as presented in their previous paper of February 08, 2007.

One topic that Applicants wish to clarify in the present paper is the amount of solvent contained in the Michael-curing compositions disclosed by Irie. Applicants maintain that wherever Irie discloses a composition that contains Michael donor and Michael acceptor, that same composition has non-reactive volatile content of 43% or higher.

In the above-identified office action (page 6), the Examiner stated,

> "Finally, in Example 31 he [Irie] exemplifies the process of
> obtaining of base coat composition using the claimed
> ingredients, Michael addition reaction, and only 7% of
> non-reactive volatile compound, such as isoproplyl alcohol
> (col. 12, line 40 through col. 13, line 2)."

Applicants respectfully submit that the Examiner's description of Irie's Example 31 is incorrect. For example, the ingredients list for Irie's base coat composition (Irie, col. 12, lines 48-64) shows that the base coat composition does not have a Michael donor. Thus the base coat composition is not capable of Michael addition reaction. Consequently, whatever the level of non-reactive volatile compound in Irie's base coat composition, that base coat composition does not have all the features of the composition recited in the present claims.

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In Irie's Example 31, Irie teaches that the base coat composition is applied and set, and "then" the solution of Irie's Example 1 is applied. The base coat composition and the solution of Example 1 are clearly two separate compositions in Irie's teachings. As discussed in detail in Applicants' previous papers, the solution of Irie's Example 1 that is used in Irie's Example 31 has at least 43% non-reactive volatile compounds.

Consequently, Applicants maintain that Irie's Example 31 does not disclose any one composition that has Michael donor and Michael acceptor and that also has less than 43% of non-reactive volatile compound.

Applicants further submit that, when Irie's entire disclosure is examined, there is no place in Irie's disclosure in which Irie teaches any composition that has Michael donor and Michael acceptor and that has less than 43% of non-reactive volatile compound. Irie characterizes compositions of his invention (i.e., those that are capable of Michael addition) as "dissolved or dispersed" in solvent, and all of Irie's examples of such comositions have at least 43% of non-reactive volatile compound.

Applicants submit that Irie's "solvent" is a non-reactive volatile compound. Solvents are, by definition, non-reactive compounds. Regarding volatility, Irie describes his compositions as "for coating use" (col. 1, line 5). It is well known that, in order for a composition to be useful as a coating, the solvent must be volatile.

Consequently, Applicants maintain that Irie does not teach or suggest compositions with Michael donor, Michael acceptor, and a level of non-reactive volatile compound lower than 43%. In contrast, the present claims recite level of non-reactive volatile compound of 5% or less. The Michael donor and Michael acceptor in Irie's compositions are dissolved or dispersed in solvent. In contrast, in the compositions of the present invention, the multi-functional Michael donor and multi-functional Michael acceptor cannot be dispersed or dissolved, because the amount of non-reactive volatile compound is too small to allow for that. Thus, the physical form of the composition of the present invention is of a different type than the physical form of the compositions disclosed by Irie. Therefore, Applicants submit that the large difference in level of non-reactive volatile compound renders the present claims non-obvious over Irie.

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### Response to rejection of claim 21 over Irie in view of Leake

In the above-identified Office Action the Examiner rejected claim 21 under 35 USC §103(a) as being obvious over US 5,959,028 (Irie) in view of US 6,521,716 (Leake).

Applicants discussed Leake in detail in their paper of April 13, 2006. As explained therein, the disclosure of Leake is limited to Michael curing compositions involving a particular set of Michael acceptors. The specific Michael acceptors disclosed by Leake are either those labeled by Leake as "doubly activated (Leake, col. 3, line 55) or else those chosen from a specific list (Leake, Abstract). Thus, a person of ordinary skill will conclude that Leake is teaching that Leake's specific Michael acceptors are required to accomplish cure without the use of catalyst.

In contrast to Leake's teaching, the multi-functional Michael acceptors of the present claims do not fall within the category of the specific Michael acceptors defined by Leake. The multi-functional Michael acceptors of the present claims have the characteristic that "each Michael acceptor functional group in said multifunctional Michael acceptor is a residue of acrylic acid, methacrylic acid, fumaric acid, or maleic acid." These acid residues may be attached to the skeleton of the multi-functional Michael acceptor through any of a wide variety of types of chemical bonds (present specification, p. 3 lines 16-26), but all of the acid residues recited in the present claims form multi-functional Michael acceptors that are different from the specific Michael acceptors defined by Leake.

Consequently, Applicants submit that, in order to combine the teachings of Irie and Leake to arrive at the features of present claim 21, a practitioner would need to discard one of Leake's required features (i.e., the specific Michael acceptors defined by Leake). Therefore, Applicants submit that it would not be obvious to combine Irie and Leake to arrive at the features of present claim 21, and thus Applicants submit that present claim 21 is not obvious over Irie in view of Leake.

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Clemens Reference - Complete Copy

On December 12, 2007, Applicants submitted an Information Disclosure

Statement that listed R.J. Clemens, Journal of Coatings Technology, vol. 61, no. 770, pp.

83-91, 1989, "Comparison of Catalysts for Crosslinking Acetoacetylated Resins Via the

Michael Reaction."

Applicants recently discovered that, by accident, the copy of this reference that

was sent with the IDS on December 12, 2007 was incomplete. A complete copy of the

reference is included herewith.



Conclusion

In view of the foregoing amendments and arguments, Applicants respectfully

request the Examiner to reexamine the claimed subject matter, to withdraw the rejections

of the claimed subject matter and to allow claims 1-6 and 11-24 at this time. If, however,

there remain any open issues which the Examiner believes can be resolved by a telephone

call, the Examiner is cordially invited to contact the undersigned agent.

No fees are believed to be due in connection with the submission of this

amendment; however, if any such fees, including petition or extension fees, are due, the

Commissioner is hereby authorized to charge them, as well as to credit any

overpayments, to Deposit Account No. 18-1850.


                                                      Respectfully Submitted,


                                                      Carl P. Hemenway

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Date:   July 03, 2007

# A Comparison of Catalysts for Crosslinking Acetoacetylated Resins via the Michael Reaction

Robert J. Clemens and F. Del Rector

Eastman Chemical Products, Inc.[*]

Thermoset coatings can be prepared at ambient temperatures from acetoacetylated resins, polyacrylates or unsaturated resins, and a basic catalyst, via the Michael Reaction. A model of this crosslinking system, the reaction of isobutyl acetoacetate and ethyl acrylate, was carefully studied to determine the effects of different catalysts. Several acetoacetylated resins were crosslinked via the Michael reaction and the physical properties of the resulting thermoset coatings were evaluated.

## INTRODUCTION

The coatings industry is continually searching for new methods of preparing thermoset polymers at ambient temperatures, and several research groups have recently examined acetoacetylated polymers in this regard. Acetoacetyl groups are amphoteric, and thus can participate in a variety of chemical transformations which might be used to modify or crosslink polymers (*Figure* 1).[1] Reagents which are known to react readily with acetoacetyl groups include amines, which react with the acetoacetyl carbonyl group; aldehydes, which react with the active methylene group; and metal ions, which chelate with the enolate anion formed by treatment of the acetoacetyl group with a base. Each of these latter methods has been used to functionalize or crosslink acetoacetylated poly-

mers at ambient temperatures. The active methylene group of the acetoacetyl functionality is also known to participate in the Michael reaction, providing yet another approach for ambient temperature crosslinking.

The Michael reaction (*Figure* 2) is the base-catalyzed addition of a carbanion (the Michael donor) to an activated olefin (the Michael acceptor) such as an acrylate ester.[2] While the Michael reaction of acetoacetylated polymers was described as early as 1956,[3] it has only recently become of interest in thermosetting coatings systems. Technology has been described for crosslinking butyl acrylate/acetoacetoxyethyl methacrylate (AAEM) copolymers with polyacrylates such as trimethylolpropane triacrylate (TMPTA) in the presence of a strongly basic catalyst at ambient temperatures.[4] The possibility of preparing high-solids coatings based on low molecular weight acetoacetate esters of simple polyols or polyester resins is intriguing. Preliminary experiments in this latter area, although promising, revealed a dramatic variation in cure rates of different systems. We therefore sought a greater general understanding of this Michael crosslinking technology, with a special emphasis on the catalysts; our efforts in this regard are the subject of this paper.
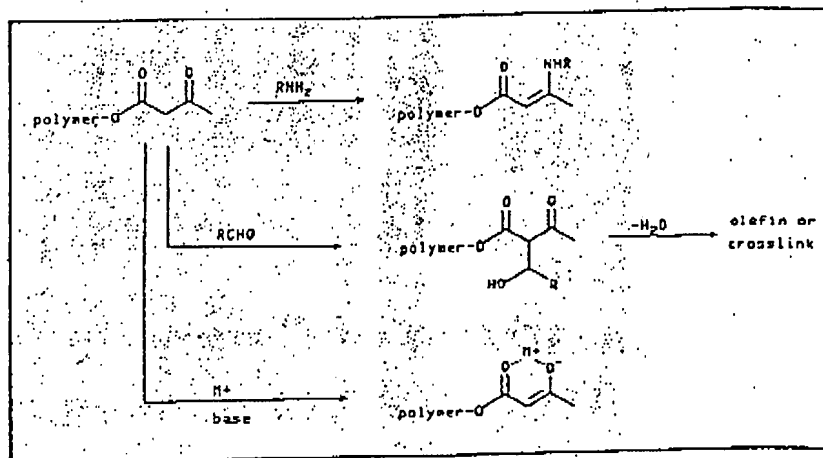
The Michael reaction is well documented in a qualitative sense for small molecules, but virtually all kinetic studies on the Michael reaction have been run with general base catalysis in buffer solutions, rather than with catalytic quantities of base in organic solvents.[5] This lack of background information, coupled with the inherent difficulties of evaluating the formation of thermoset coatings on a molecular level, led us to study a model system. Our model system provided us with a greater understanding of the crosslinking process which is effected via the Michael reaction and also facilitated the evaluation of new catalysts.

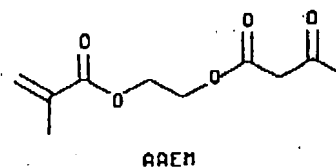R.J. CLEMENS and F.D. RECTOR



Figure 1—Acetoacetyl groups

## THE MODEL SYSTEM

Isobutyl acetoacetate [(1) in *Figure* 3] was selected to model an acetoacetylated polyester derived from neopentyl glycol or cyclohexanedimethanol, and ethyl acrylate [(2) in *Figure* 3] was used to model the TMPTA. Compounds 1 and 2 were dissolved in n-butanol (nBuOH), tetrahydrofuran (THF), or xylene, at concentrations which approximated the concentrations (1 M) of the two functional groups in a high solids coatings system; the resulting solutions were carefully equilibrated at 25°C (77°F). A catalyst was added to each solution, and aliquots were periodically withdrawn, neutralized, and analyzed by gas chromatography (see Experimental section for further details). In sample runs with 5 mole% (relative to acetoacetyl groups) of benzyltrimethyl ammonium methoxide or KOH as the catalyst, the formation of both a mono (3) and a bis-Michael adduct (4) was observed (*Figure* 3). The reaction proceeded until virtually all of the ethyl acrylate was consumed (*Figure* 4).

Analysis of the data from a series of model reactions suggested that the rate of the Michael reaction had a first order dependency on the acrylate concentration, but was independent of the concentration of the isobutyl acetoacetate (1). Indeed, the rate of reaction was unchanged when the acetoacetate concentration was reduced ten-fold. This data is consistent with a reaction mechanism in which the deprotonation of the acetoacetate ester is rapid and af-

fords a steady-state concentration of the reactive enolate anion (5) (*Figure* 5). The model reaction is more complex than might be surmised from the apparent first order nature of the process since, after the reaction has started, there are two acetoacetate anions [(5) and (7)] competing for the ethyl acrylate. From a coatings development standpoint, however, the rate of Michael reaction of ethyl acrylate is the critical factor; each molecule of ethyl acrylate consumed in the model system corresponds to the formation of a branch point or a crosslink in an actual resin formulation. A more detailed picture of the overall mechanism is presented in *Figure* 5;* several acid-base equilibria, particularly anion protonation by the solvent or other acetoacetate species, have been omitted for clarity.



AAEM

Our model system showed the rate-limiting step of the Michael reaction to be dependent upon the acrylate (1)
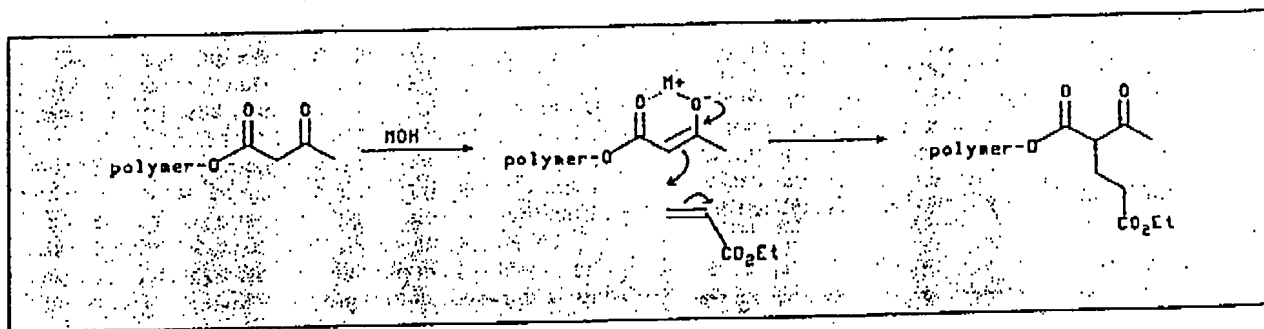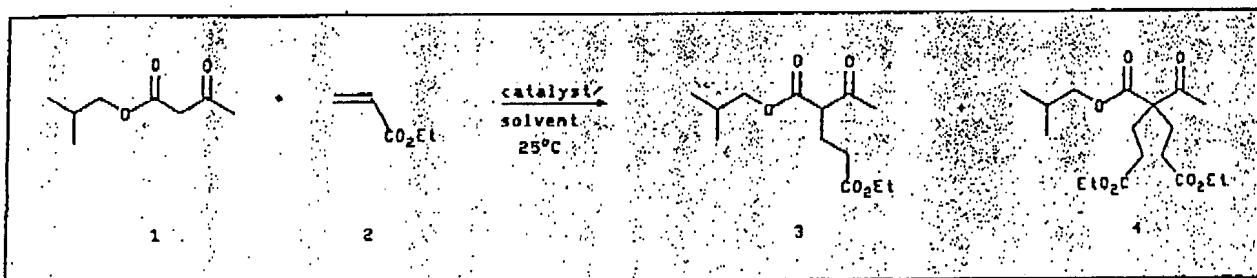
Figure 2—Michael reaction

Figure 3—Formation of both a mono (3) and a bis-Michael adduct (4) as a result of sample runs with 5 mole% (relative to acetoacetyl groups) of benzyltrimethyl ammonium methoxide or KOH as the catalyst

and acetoacetate anion (5) concentrations. In coatings systems, adjustment of the acrylate concentration would be limited by stoichiometric considerations and could not be used to control the rate of crosslinking. The dependence of the reaction rate on the acetoacetate anion concentration, however, was quite promising since the concentration of this anion could be varied by both the amount of catalyst which was used and by the initial deprotonation equilibrium ($k_1/k_{-1}$). We therefore planned to examine the effect of a variety of bases on this deprotonation equilibrium via our model system.

The appearance of a bis-Michael adduct in our model reactions was relevant to subsequent work; it greatly complicated kinetic analysis of the model system and implied that less than an equivalent of the acetoacetate functionality was required relative to the acrylate. More importantly, coatings formulations in which large amounts of the bis-Michael adducts were formed would be expected to cure faster and to gel sooner than those in which only mono-Michael adducts were produced. The Carothers equation was used to predict the extent of reaction necessary to achieve infinite molecular weight as a function of the number of reactive functional groups which were present on the resin and on the crosslinking reagent.[6] This latter information is important when considering the pot life of various systems (note that a bifunctional crosslinking reagent would be expected to provide a much longer pot life than a tetrafunctional one for a given catalyst system). A graphical rendition of the Carothers equation (*Figure 6*) was used to predict the extent of reaction for which our model system might be expected to approximate the solution chemistry in actual coatings systems.*

state concentrations of the anion. We selected commercially available amidine and guanidine bases (*Table 1*) which had $pK_b$ values intermediate between hydroxide and triethylamine for our studies. The active methylene protons on acetoacetate esters have a $pK_a$ of ~12, and the methine proton of the mono-Michael adduct (3) has a $pK_a$ of ~13, so these bases were expected to vary the deprotonation equilibria and, consequently, the relative concentration of the acetoacetate anion. It was expected that the hydroxide bases would rapidly deprotonate the acetoacetate ($k_1 >> k_{-1}$ or $k_2$) and thus establish a limiting velocity for the Michael reaction under the conditions of our model system. This limiting rate appeared to be 30 × $10^{-5}$ sec$^{-1}$ (*Figure 7*).*

As shown in *Figure 8*, TMG was found to be an effective catalyst for the Michael reaction of our model system, and was also found to be less sensitive to the reaction solvent than KOH. It also catalyzed the Michael reaction less effectively, as was predicted.

The relative reaction rates which resulted from using the various bases in our model system are shown in *Table 2*, and the effect of various catalyst concentrations on the rate is shown in *Table 3* and *Figure 9*. Rate constants over

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*The reaction rates are presented as pseudo-first-order rate constants, as determined from the slope of a plot of log [EA] vs time, as derived from the integration of the rate expression d[EA]/dt = $k_{on}$[EA], where $k_{on}$ is a function of the concentration of the base (held constant), the deprotonation equilibrium constant (or a given base), and the rate constants $k_2$ and $k_3$ (at later stages of the reaction). Qualitative observations suggest $k_2 > k_3$, but the impact of this second process is only seen later in the reaction as (3) builds up, and is lessened by the higher pKa of the methine proton of 3. A rigorous study of our model system would require separating $k_2$ and $k_3$, but would have provided little additional information to our coatings application.
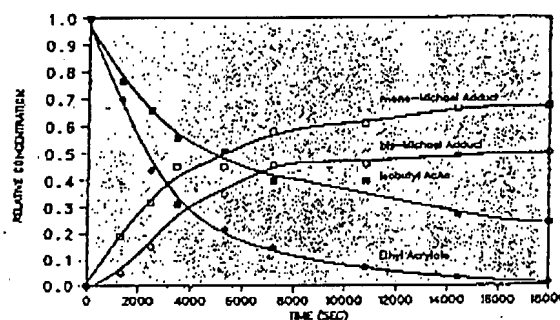
## EVALUATION OF CATALYSTS

It is known that Michael reactions between acetoacetate esters and acrylates occur readily at 25°C with strong bases such as methoxide and hydroxide, but not with weaker organic bases such as triethylamine.[7] This can be explained by the position of the deprotonation equilibrium ($k_1/k_{-1}$), in which weaker bases afford lower steady-

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*Implicit in our model study is the assumption that the model system reflects the kinetics of the curing process in its early stages.
[dagger]Triethylamine will promote Michael reactions at elevated temperatures.



Figure 4—Michael reaction of the model system; KOH catalyst (5 mole%); 25°C
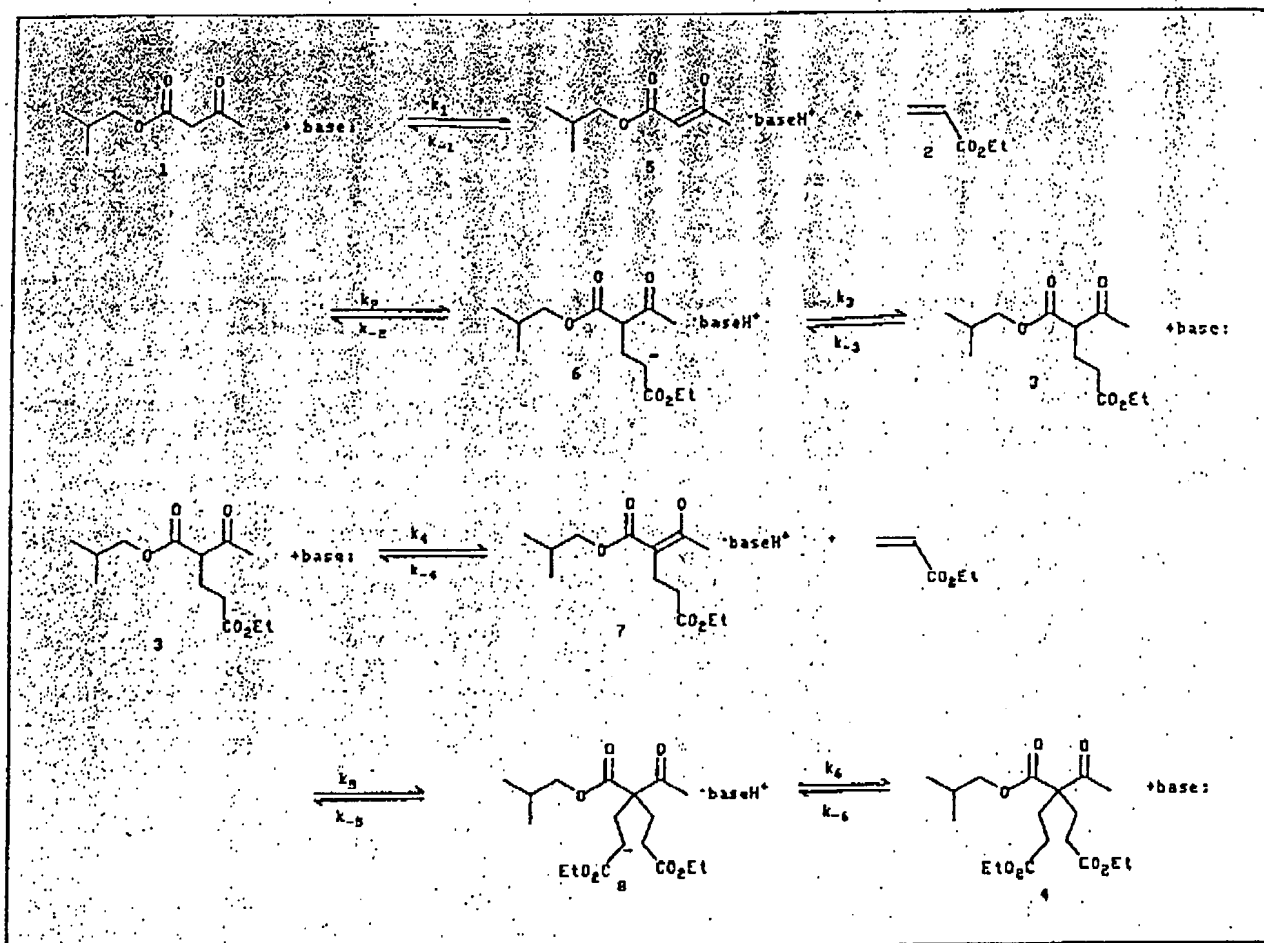
R.J. CLEMENS and F.D. RECTOR



Figure 5—Overall reaction mechanism

$20 \times 10^{-3}$ sec$^{-1}$ in our model system usually correlated with extremely short pot lives in actual coatings systems, while rate constants less than $2 \times 10^{-5}$ sec$^{-1}$ could not be expected to provide effective cure in a coating.

The results in *Table* 3 show that amidine and guanidine bases are clearly effective catalysts for the Michael reac-

tion;[7] TMG and DBU provided the lower reaction rates which were expected as $k_{-1}$ became larger relative to $k_1$. The rate of reaction achieved with the DBN was unexpected and is not yet fully understood; possibly the pK$_b$ of DBN in our system was higher than anticipated. At 25°C, and at 5-10% levels, neither triethylamine, 1,4-diazabicyclo(2.2.2)octane (DABCO), nor 4-dimethyl-
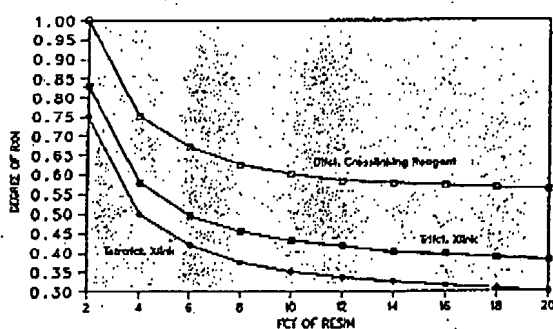


Figure 6—Degree of reaction at gel point (by Carothers equation)

Table 1—Basicity of Some Commercially Available Catalysts For the Michael Reaction



|         | TMG | DBU | DBN |
|---------|-----|-----|-----|

| Base | Class | pK$_b$ |
|------|-------|------|
| Triethylamine (Et$_3$N) | amine | 10.7 |
| 1,8-Diazabicyclo(5.4.0)undec-7-ene (DBU) | amidine | 12.5 |
| 1,5-Diazabicyclo(4.3.0)non-5-ene (DBN) | amidine | 12.7 |
| Tetramethylguanidine (TMG) | guanidine | 13.6 |
| Sodium hydroxide (NaOH) | hydroxide | ~14 |

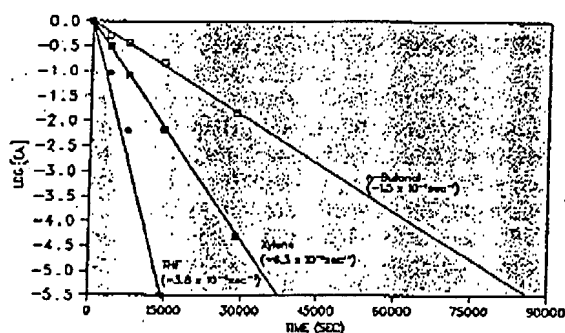Figure 7—Michael reaction of the model system; TBAH catalyst (5 mol%); 25°C



Figure 8—Michael reaction of the model system; TMG catalyst (5 mol%); 25°C

aminopyridine (DMAP) would catalyze the Michael reaction; all of these compounds are basic catalysts of relatively low $pK_b$. As expected, the rate of the Michael reaction increased with increasing catalyst levels; with TMG, the correlation between the rate of reaction and the catalyst level (1-8 mole%) was nearly linear.

The relative amount of the bis-Michael adduct (4) which was produced varied considerably between the different types of catalysts. As discussed previously, formation of the bis-adduct would accelerate curing in an actual coatings system. If measured when half the ethyl acrylate was consumed, the amidine bases DBU and DBN provided bis/mono adduct ratios (4/3) of about 0.7, which was far higher than the bis/mono adduct ratio of 0.04 achieved with the hydroxide bases. TMG was closer to the amidines, with a bis/mono-adduct ratio of 0.3. Thus, at catalyst concentrations which provided equal rate constants, the amidine and guanidine catalysts would be predicted to provide more densely crosslinked systems than the hydroxide bases, partially at the expense of pot life.

The Michael reactions of isobutyl acetoacetate with several other activated olefins (Michael acceptors) were briefly examined to establish a general order of reactivity. Ethyl acrylate was clearly the most reactive olefin studied, but diethyl maleate also reacted readily. Methyl methacrylate (MMA) and ethyl crotonate were notably less reactive, while ethyl cinnamate barely participated in TMG-catalyzed Michael reactions at ambient temperatures.

Two acetoacetylated acrylic resins were synthesized by the radical-promoted, solution polymerization of AAEM with MMA. The physical properties of these copolymers, containing 20 and 30 mol% AAEM, respectively, are summarized in Table 4. These resins had significantly reduced solution viscosities and glass transition temperatures when compared with MMA or MMA/hydroxyethylmethacrylate (HEMA) copolymers; this was an expected and desirable result of introducing bulky pendant groups onto the polymer backbone.

In the first of the aforementioned series of gel point experiments, our 20 mol% AAEM/MMA copolymer (fw 614/acetoacetyl group) and TMPTA were dissolved in 50/50 butanol/xylene to afford a solution (36% solids) which was 0.5 M in both acetoacetate and acrylate functionality. The addition of 2.5 mol% (relative to the acetoacetyl groups) TMG catalyst gelled this solution in six hours (Table 5); doubling this catalyst level to 5 mol% reduced the gel time by a factor of 3, to two hours. Gel times could be shortened by replacing the 5 mol% TMG (gel time = 6 hr) with a similar concentration of DBN (3 hr) or TBAH (4 hr), or lengthened with DBU (22 hr), which was consistent with predictions from our model study and mechanistic analysis. The gel time could be shortened by the addition of excess TMPTA; doubling the TMPTA concentration reduced the gel time by a factor of ~1.5.

Little dependence on the concentration of the acetoacetylated polymer was observed (in the 0.1-1 M range), and in several cases the more dilute samples gelled faster.

Application of the Carothers equation indicated that the number of functional (acetoacetyl) groups per polymer

## PREPARATION OF THERMOSET MATERIALS—GEL POINT EXPERIMENTS

Our catalyst evaluation was extended to the preparation of thermoset materials, via the ambient temperature crosslinking of acetoacetylated acrylate, polyester, and cellulosic materials. This evaluation of Michael crosslinking technology occurred in two distinct technical phases. First, a series of gel time experiments was used to determine the general versatility of the Michael approach to crosslinking; the crosslinking of two acrylic, AAEM-based resins was then examined in greater detail.
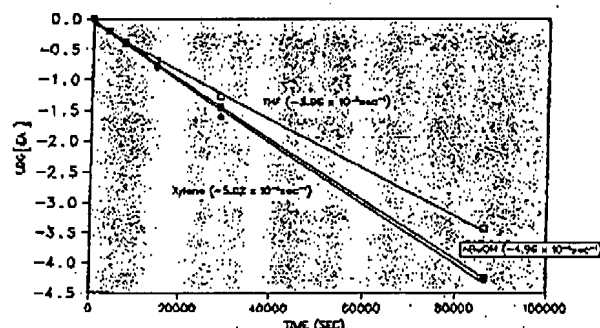
Table 2—Pseudo-First-Order Rate Constants, Five Mole% Catalyst ($\times 10^3$ sec$^{-1}$)

| Catalyst | Solvent | | | |
|---|---|---|---|---|
|  | THF | Xylene | nBuOH | EEP |
| KOH | 29 | insol. | .20 | — |
| nBu₄NOH | 30 | 10.5 | 6.3 | — |
| TMG | 5.8 | 5.0 | 7.7 | 8.3 |
| DBU | 2.8 | 2.7 | 3.7 | — |
| DBN | 29 | — | — | — |
| Et₃N | <0.1 | — | — | — |

Table 3—Effect of Catalyst Concentration on the Rate of
Michael Reactions
THF, 25°C

| Catalyst | Concentration | Rate ($x\ 10^3\ sec^{-1}$) |
|---|---|---|
| nBu₄NOH (TBAH) | 5% | 30 |
|  | 2 | 4.6 |
| TMG | 10 | 21 |
|  | 8 | 7 |
|  | 5 | 5.8 |
|  | 4 | 4.4 |
|  | 2 | 1.0 |
|  | 1 | 0.5 |
| DBU | 5 | 2.8 |
|  | 2 | 0.1 |
| DBN | 5 | 29 |
|  | 2 | 2.7 |

molecule would also affect coatings cure, especially on materials with 2-20 functional groups. It was also anticipated that the concentration of both functional groups would become important as the acrylate groups became attached to the polymer and thus became less mobile; effective crosslinking would then depend on the physical proximity of functional groups. This dependency was observed by the comparison of a 10 mole% AAEM/MMA copolymer with the 20 mole% AAEM/MMA copolymer described previously; at identical concentrations of all functional groups, the less functionalized polymer required four times longer to gel (6 vs 24 hr). This result also established that our model system could be used to predict relative reactivities of different Michael systems and catalysts, but was not itself sufficient to predict cure times for different polymer systems.

The importance of functional group accessibility became even more apparent with acetoacetylated polyester resins and cellulosic polymers. These materials were prepared by acetoacetylating pendant hydroxyl groups on the polymers with diketene or methyl acetoacetate. In these polyesters and cellulosics, the acetoacetyl groups were attached directly to the polymer backbone without the benefit of a spacer group as is present in AAEM, and this was reflected in slower cure rates under conditions similar to those used with the AAEM/MMA copolymers. Furthermore, the gel time of polymers with more hin-

dered acetoacetyl groups appeared to decrease more rapidly with decreasing functional group concentrations than was the case with the AAEM based polymers. It was possible to offset the slower rates by increasing the concentrations of both functional groups via higher solids formulations. This approach was greatly simplified by the viscosity-reducing properties of the acetoacetyl group. Increasing the number of acetoacetyl groups per molecule was also found to enhance cure rates, especially with lower molecular weight species.

Cellulose triacetoacetate was readily crosslinked with TMPTA, while several less highly acetoacetylated cellulose esters (mw~12500/acetoacetyl group) could not be gelled. In an alternate approach to crosslinked cellulosic systems, TMG was used to catalyze the crosslinking of an acryloylated cellulosic with glycerol trisacetoacetate; crosslinking occurred, as demonstrated by sample gellation within one hour. This "reverse" approach to Michael-type crosslinking should be readily extended to make other coatings systems.

## PREPARATION OF COATINGS BASED ON ACETOACETYLATED RESINS

The two AAEM/MMA copolymers which were previously discussed were selected for a more thorough examination. DBU was selected as the catalyst which would provide the greater cure latitude and the longer pot lives which were one of our initial objectives. Cure response curves (Figure 10) were determined for both resins, using a stoichiometric amount of TMPTA as the crosslinking reagent, at four different catalyst levels.

The response curves were determined by hourly viscosity measurements; that level of catalyst which would provide a pot life of greater than eight hours and still afford complete cure was sought. Consistent with earlier observations, the higher degree of functionality on the 30 mol% AAEM resin resulted in complete cure at markedly lower levels of catalyst. For the resin containing 20 mol% AAEM, 2 mol% of DBU (relative to the acetoacetyl groups) gave the desired pot life and also effected complete cure, while 1 mole% of DBU was sufficient to cure the resin which contained 30 mole% AAEM. These catalyst levels are quite low when viewed as a percentage of the total coatings formulation (0.07-0.11%), and were used for the remainder of the coatings evaluations. The
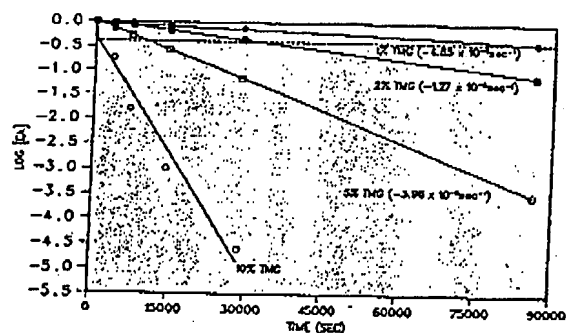


Figure 9—Michael reaction of the model system; TMG catalyst; 25°C

Table 4—AAEM/MMA Copolymers and Properties

|  | Resin (mol% AAEM) | | |
|---|---|---|---|
|  | 0 mol%[a] | 20 mol% | 30 mol% |
| Wt% AAEM | 0 | 34.9 | 47.8 |
| $M_n$ | 9590 | 6970 | 7650 |
| $T_g$ (°C) | 105 | 57 | 52 |
| % Solids | 59.0 | 57.7 | 58.0 |
| Brookfield viscosity (cP × 10³) | 471 | 42 | 24 |

(a) MMA control.

specific formulations which were tested are described in *Table* 6. It should be noted that these resins were selected simply to provide a general indication of the potential of this technology, and were not formulated to enhance any particular properties.

The premixed ingredients were sprayed onto cold-rolled steel panels which had been pretreated with Bonderite® 37, and the coatings were then allowed to cure for seven days at ambient temperature. The performance properties of the resulting AAEM-based enamels were evaluated (*Table* 7) and found to have good overall coatings performance, particularly with respect to stain resistance. The major problem which was encountered was the relatively poor hydrolytic stability, as seen in Cleveland humidity tests. It was reasoned that the amidine base which remained in the coating would catalyze the hydrolysis of the crosslinked film. Indeed, a low temperature bake (100-120°C) improved the hydrolytic stability of the coating to the point that the coatings easily passed 500 hr of Cleveland humidity testing. A more volatile amidine catalyst, a catalyst neutralization scheme, or a catalyst less effective at ester hydrolysis may provide further enhancements in the technology of Michael-cross-linked coatings.

## EXPERIMENTAL
### Model System—Typical Procedure

A stock solution of isobutyl acetoacetate (7.9 g, 0.05 mol), ethyl acrylate (5.41 mL, 0.05 mol), and 0.5 g of p-dichlorobenzene (internal standard) was diluted to

Bonderite is a registered tradename of Parker Rust Proof Co.

**Table 5—Preparation of Thermoset Materials via the Michael Reaction**

| Resin | [AcAc][a] | Catalyst | Conc.[b] | Solvent | Gel Time (hr) |
|---|---|---|---|---|---|
| Polyester[c] | .80M | KOH | 1[f] | nBuOH/ xylene | 1 |
| " | | TMG | 5 | " | 1 |
| " | | TMG | 2 | " | 17 |
| " | | TMG | 1 | " | no gel |
| " | | DBU | 5 | " | 1 |
| CHDM (AcAc)₂ | .50M | TMG | 10 | " | 6 |
| 10% AAEM/ MMA[d] | .27M | TMG | 5 | " | 25 |
| | .21M | TMG | 10 | acetone | 1 |
| 20% AAEM/ MMA | .25M | TMG | 5 | nBuOH/ xylene | 6 |
| " | | TBAH | 5 | " | 4 |
| " | | DBN | 5 | " | 3 |
| " | | DBU | 5 | " | 22 |
| Cellulose (AcAc)₂ | .33M | TMG | 5 | acetone | 2 |
| | .10M | TMG | 5 | " | 1 |
| Cellulose acrylate[e] | .25M | TMG | 5 | " | 2 |
| | .20M | TMG | 10 | EEP | 1 |

(a)Concentration of acetoacetyl (AcAc) groups in solution.
(b)Catalyst concentration in mol% relative to acetoacetyl groups.
(c)DMCD/NPG/TMP IPA resin, Mw 6000, 400 OH group, 90% acetoacetylated.
(d)10 mol% AAEM in monomer feed; see Experimental section.
(e)Cellulose acetate butyrate, acylated with acryloyl chloride (one 400/acryloyl group); crosslinked with glycerol trisacetoacetate

50.00 mL with THF. A 10.00 mL volumetric flask was filled with a portion of this solution and immersed in a Haake constant temperature bath whose contents were maintained at 25.0 ± 0.1°C. TMG (5 mole%, 0.063 mL) was added to the thermally equilibrated solution and the flask was agitated. Reaction aliquots (0.5 mL) were re-
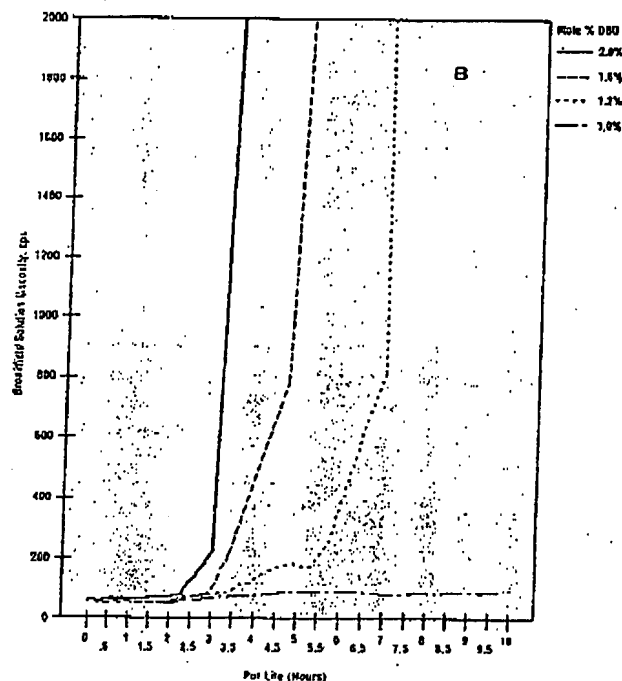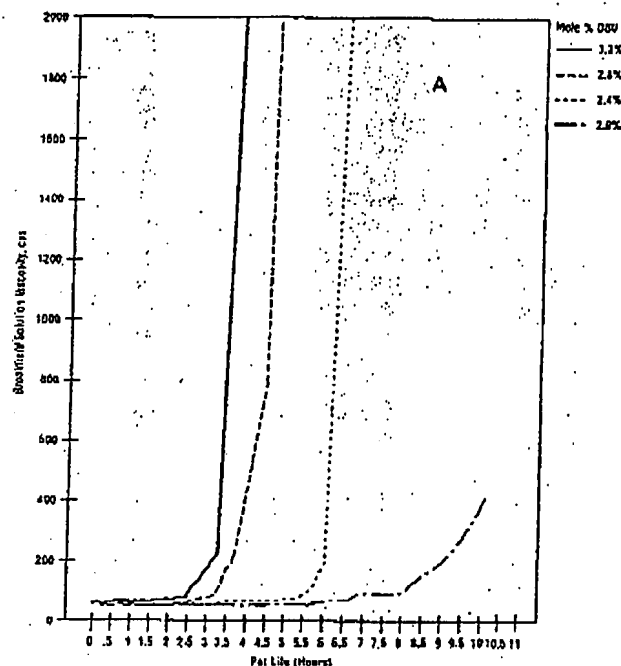




Figure 10—A: Michael addition, DBU catalyst, 20 mole% AAEM resin, pot life. B: Michael addition, DBU catalyst, 30 mole% AAEM resin, pot life

moved at Time = 0, and then at 30-60 min intervals for the next eight hours. These aliquots were added to a vial which contained 2.00 mL of diethyl ether and 0.200 mL of 0.1N HCl, and the vials were thoroughly shaken and the phases allowed to separate. A portion of the ethereal layer was transferred to a sample vial for GC analysis. Control experiments established that the extraction procedure completely quenched the Michael reaction and that the relative amounts of the reactants (except the catalyst), the products, and the internal standard were unchanged by the extraction procedure. The samples were than autoinjected (HP7673A) onto a 30 m DB-5 capillary column in an HP5890 gas chromatograph (injector 220°C; oven 70°C for 2 min, then + 20°C/min to 240°C) equipped with a flame ionization detector. Each sample was injected twice, and the integrated values of the peak size versus the internal standard were averaged. The log [ethyl acrylate] was plotted as a function of time to calculate a pseudo-first-order rate constant in sec⁻¹. With those reactions which were fast enough to progress beyond pseudo-first-order behavior, the data obtained during the first half-life of ethyl acrylate was used to reflect the rate while the model was simulating coatings cure. All individual lines had regression coefficients ($R^2$) >0.970, but repeated runs of "identical" reactions suggested that the precision of any given measurement was ~20%.

## Preparation of Acrylic Resins

A heated, four-necked round-bottomed flask with electronic temperature control was equipped with an air driven stirrer, a condenser, and an addition funnel. The resin formulation was calculated so as to provide a final product at 60% solids. The majority of the Ektapro® EEP solvent was charged into the nitrogen purged flask, and was then heated to 100°C. The monomers and Vazo® 67 initiator were dissolved in Ektapro EEP solvent, placed in the addition funnel, and added dropwise to the heated solvent over four hours. After the addition was complete, the reaction was maintained at 100°C for an additional half-hour; and additional ½ mole% of the initiator (as a

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Ektapro is a registered tradename of Eastman Chemical Products.
Vazo is a registered tradename of E.I. duPont de Nemours & Co., Inc.

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### Table 6—Enamel Formulations Based on Michael-type Crosslinking

| Part A: Grind | Resin (Mole% AAEM) 20 | 30 |
|---|---|---|
| Resin (60 wt% in Ektapro EEP solvent) | 43.6 | 32.6 |
| Trimethylolpropane triacrylate | 3.6 | 4.3 |
| TiO₂ | 20.4 | 15.2 |
| MIAK | 14.4 | 17.8 |
| Ektapro EEP solvent | 7.9 | 14.4 |
| n-Butanol | 7.9 | 14.4 |
| **Part B: Catalyst** | | |
| DBU (5 wt% in n-butanol) | 2.2 | 1.3 |
| | 100.0 | 100.0 |
| #4 Ford Cup viscosity, sec | 30 | 32 |

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### Table 7—Properties of Enamel Formulations Based on Michael-type Crosslinking

| | Resin (Mole% AAEM) 20 | 30 |
|---|---|---|
| Average film thickness, mil | 1.2 | 1.2 |
| Gloss at 60° | 83 | 82 |
| at 20° | 74 | 70 |
| MEK rub resistance | | |
| Number passed | 250 | 250 |
| Pencil hardness to mar | 4H | 3H |
| Impact resistance, in.-lbs | | |
| Direct | 8 | 18 |
| Reverse | 4 | 4 |
| Stain resistance[a] | | |
| Iodine after 5 min | N | N |
| Iodine after 30 min | N | VS |
| Ink after 24hr | N | N |
| Chemical resistance[a] | | |
| Sulfuric acid after 1 hr | N | N |
| Sodium hydroxide after 1 hr | N | N |

(a)Scale: N = no effect; and VS = very slight effect.

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10 mol% solution in Ektapro EEP) was added to conclude the reaction. The solution of the polymer in Ektapro EEP was then cooled for storage.

## Preparation of Thermoset Materials

An acetoacetylated polymer* and a stoichiometric quantity (based on individual functional groups) of TMPTA were dissolved in either EEP or 50/50 nBuOH/xylene at the specified concentration (typically 33% solids). Aliquots (10 mL) of these stock solutions were pipetted into 15 mL vials, a catalyst was added (typically 5 mole% relative to acetoacetyl groups), and the vials were repeatedly inverted until they gelled. A visible viscosity increase was generally noted only very shortly before the gel point.

## SUMMARY AND CONCLUSIONS

A model system was developed to evaluate catalysts for the Michael reaction of acetoacetylated compounds and to learn more about the reaction process. This model was used to demonstrate that alkylated amidine (DBU, DBN) and guanidine (TMG) bases will catalyze the Michael reaction at ambient temperature, and that reaction rates can be controlled by the choice of the catalyst and the level at which it is used. This discovery provides an alternative to the more conventional hydroxide bases, although each class of catalysts has its own merits. The hydroxide bases are the low cost materials and are extremely reactive, but they suffer from lesser solubility in nonpolar solvents. Also, the hydroxide bases are often

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*Hydroxyl groups were acetoacetylated at 45°C, typically in ethyl acetate solution, with DMAP catalyst via the slow addition of diketene.[1]

used at very low levels, which increases the susceptibility of these systems to catalyst neutralization by acidic impurities. The advantages of the alkylated amidines and guanidines include their ready solubility, even in xylene, and the diversity provided by the wide variety of materials available within these compound classes.

We have demonstrated that amidine and guanidine catalysts will promote the ambient temperature crosslinking of acetoacetylated acrylate, polyester, and cellulosic polymers via the Michael reaction. In an extension of the Michael crosslinking technology, we crosslinked an acryloylated cellulosic polymer with a trisacetoacetate using TMG. Many acetoacetylated polymers and polyols are readily amenable to high solids application, and the Michael reaction is accelerated under these conditions; the catalyst must be carefully chosen to provide the best balance between cure rate and pot life.

Much remains to be learned about the Michael reaction, especially as it applies to the preparation of thermoset coatings. We hope that others will build on our efforts to understand this reaction and can develop practical coatings technology based on the Michael reaction of acetoacetylated monomers and polymers.

### References

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